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SOLID-STATE HIGH-RESOLUTION ^{29}Si NMR OF FELDSPARS: Al–Si DISORDER AND THE EFFECTS OF PARAMAGNETIC CENTRES

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ABSTRACT

High-resolution ^{29}Si nuclear magnetic resonance spectra obtained by magic-angle spinning are specific to each type of low-temperature plagioclase and alkali feldspar. Microcline and albite each give three well-resolved resonances, corresponding to the T_1m, T_2O and T_2m Wyckoff positions populated by silicon, but at different peak-positions, reflecting the difference between the two structures. The spectrum of a perthite is a superposition of well-resolved microcline and albite peaks. The three resonances of calcic plagioclase occur at lower applied magnetic field, reflecting the substitution of aluminum for silicon, and they are broader, indicating Al–Si disorder. The natural high-temperature feldspars orthoclase and labradorite give two broad peaks of similar intensity, consistent with the two equally populated T Wyckoff positions in their structures. Similar broadening of peaks, observed with samples of well-ordered feldspar heated at 1100°C, is indicative of considerable Al–Si disorder. Paramagnetic ions such as Fe^{2+} and Fe^{3+} cause broadening of the signals attributed to nearby silicon atoms and shorten the time taken for spin-lattice relaxation of these atoms. Since typical intervals between radiofrequency pulses are much less than the relaxation time of the Si atoms remote from a paramagnetic centre, broad signals from the relatively few silicon atoms near such centres can become predominant in the spectrum. Hence, in systems containing paramagnetic ions, longer intervals between pulses give better resolved spectra. Other potentially perturbing factors, such as the presence of mineral inclusions, have a negligible effect.

Keywords: feldspar, ^{29}Si nuclear magnetic resonance, magic-angle spinning, paramagnetic ions, inclusions.

SOMMAIRE

Chaque type de plagioclase et de feldspath potassique de basse température possède un spectre spécifique de résonance magnétique nucléaire ^{29}Si que l'on obtient par spinning à l'angle magique. Albite et microcline montrent trois résonances bien nettes, correspondant aux positions Wyckoff T_1m, T_2O et T_2m occupées par le silicium, mais qui se présentent à des positions différentes du maximum et reflètent ainsi la différence entre les deux structures. Le spectre d'une perthite résulte de la superposition de pics bien résolus du microcline et de l'albite. Les trois résonances du plagioclase calcique se présentent dans un champ magnétique appliqué moins intense, vu la substitution d'aluminium au silicium; elles sont plus larges, témoignant ainsi d'un désordre Al–Si. Pour l'orthose et la labradorite, feldspaths naturels de haute température, il y a deux pics larges d'intensité semblable, ce qui concorde avec la présence dans la structure de deux positions de Wyckoff T d'égale population. Un élargissement semblable des pics, observé dans les échantillons de feldspath bien ordonné chauffés à 1100°C, révèle un désordre Al–Si considérable. Les ions paramagnétiques, tels que Fe^{2+} et Fe^{3+}, causent un élargissement des signaux attribué aux atomes de Si voisins et raccourcissent le temps que mettent ces atomes à accomplir la relaxation du réseau de spin. Vu que le laps de temps entre les pulsations de radiofréquence est beaucoup plus court que le temps de relaxation des atomes de Si éloignés d'un centre paramagnétique, des signaux larges venant d'un nombre relativement petit d'atomes de Si proches de ces centres peuvent devenir prédominants dans le spectre. Il s'ensuit que dans les systèmes qui contiennent des ions paramagnétiques, un intervalle plus long entre les pulsations améliore la résolution spectrale. L'influence des autres facteurs, telle la présence d'inclusions minérales, est négligeable.

(Traduit par la Rédaction)

Mots-clés: feldspath, résonance magnétique nucléaire ^{29}Si, spinning à l'angle magique, ions paramagnétiques, inclusions.

INTRODUCTION

Since Lippmaa *et al.* (1980, 1981) showed that detailed structural information is available from ^{29}Si magic-angle-spinning (MAS) nuclear magnetic resonance (nmr) spectroscopy of silicate minerals, this has become an important technique in mineralogy (Wasylishen & Fyfe 1982, Fyfe *et al.* 1983a). MAS nmr is a direct probe of the local environment of magnetic nuclei in many instances where the atom of interest does not respond to other direct techniques (Hawthorne 1983).

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Silicon atoms at a given site in framework aluminosilicates show up to five ^{29}Si nmr peaks between -80 and -111 ppm, each corresponding to a different arrangement of aluminum atoms in the nearest-neighbor *T* sites, *i.e.*, to a variation of *n* from 0 to 4 in the configuration $^{29}\mathrm{Si(OAl)}_n\mathrm{(OSi)}_{4-n}$. The position and intensity of these peaks give direct information about the local environment around the silicon atom (Lippmaa *et al.* 1980, 1981, Mägi *et al.* 1984). Where more than one crystallographically nonequivalent site is present, each crystallographically nonequivalent silicon can provide its own set of up to five peaks. Bond angles and bond lengths also have an effect on chemical shift (Smith *et al.* 1983, 1984), and work continues on the relationship of chemical shifts to structural parameters (Smith *et al.* 1984). The probability of finding silicon and aluminum atoms at next-nearest *T* sites also has an appreciable effect on chemical shift, such that Al–Si disorder in these more remote sites leads to peak broadening, as has been shown in zeolites (Fyfe *et al.* 1983b, 1984). Thus in the absence of other causes of broadening, broadening of the ^{29}Si MAS nmr peaks in aluminosilicates implies Al–Si disorder.

Most natural minerals contain paramagnetic impurities, exsolution textures, intergrowths, inclusions and alteration products; any broadening due to such features could be mistaken for Al–Si disorder. We have chosen feldspars to investigate such effects (Williams & Hartman 1983, 1984, Williams 1984). *Note added in proof:* ^{29}Si MAS nmr spectra of feldspar similar to those presented here have recently been reported by Kirkpatrick *et al.* (1985).

EXPERIMENTAL

The ^{29}Si MAS nmr spectra were obtained on powdered minerals using a Magic Angle Spinning probe (Fyfe *et al.* 1982) and "Delrin" or "Perspex" rotors, on a Bruker WH–400 multinuclear Fourier Transform nmr spectrometer equipped with a 9.4 Tesla superconducting magnet. The spectra were recorded at a frequency of 79.46 MHz, with 8K data points, using a spectral width of 25,000 Hz and a 5 μs pulse width; they were Fourier-transformed with a line broadening of 50 Hz. The samples were spun at approximately 3500 Hz at an angle of 54.7° to the magnetic field. With many samples, a good signal-to-noise ratio was obtained after 200 scans with a 5 s relaxation delay between scans. However, especially pure samples (*e.g.*, BLW150: Amelia albite) gave much better spectra with relaxation delays of up to 300 s, indicating long ^{29}Si spin-lattice relaxation times. Relative positions of the ^{29}Si peaks (chemical shifts) are reproducible to ± 0.1 ppm and are reported in parts per million (ppm) to low magnetic field of tetramethylsilane (*i.e.*, negative values refer to peaks to a higher magnetic field). The nmr parameters and relevant data are given in Table 2 for plagioclase and Table 3 for alkali feldspar. The localities and donors of the samples are given in Table 1.

The anorthite content of the plagioclase specimens was calculated from the indices of refraction of cleavage fragments measured using immersion oils (Moorhouse 1959) and confirmed using a three-axis universal stage (Moorhouse 1959) on standard thin sections. Chemical analyses were done using a Philips 1450 X-ray-fluorescence spectrometer with rhodium tube, and calibrated with USGS standard rocks.

All heating was done in a muffle furnace at atmospheric pressure, on approximately 3 g of powdered mineral in platinum crucibles. Microcline and oligoclase were heated at 1100°C and removed for ^{29}Si MAS nmr analysis after 1, 8, 12, 20 and 28 days.

TABLE 1. LIST OF MINERAL SPECIMENS

Number	Mineral	Locality, Acquisition Number	Donor	% Fe_2O_3*
BLW004	Microcline	Gibraltar Point, Parry Sound, Ontario		0.58
BLW031	Microcline	Non loc.	Brock University	0.30
BLW036	Oligoclase	M-18-8-2 Tvedestrand, Norway	Brock University	0.16
BLW038	Bytownite	M-18-11-1 Crystal Bay, Minnesota, U.S.A.	Brock University	0.36
BLW056	Plagioclase + quartz	3507 Azores	W. T. Jolly	0.40
BLW080	Labradorite	BAN (K), Gabbro, Sierra Leone	H. R. Williams	1.02
BLW083	Orthoclase	Good Springs, Nevada	P. A. Peach	0.56
BLW123	Microcline	M3614 Hungry Lake Mine, Chapton To., Parry Sound, Ontario	Royal Ontario Museum	0.08
BLW124	Microcline	M36146 Brignall Mine, Conger To., Parry Sound, Ontario	Royal Ontario Museum	0.10
BLW128	Albite	M36070 Purby Mine, Mattawan To., Nipissing, Ontario	Royal Ontario Museum	0.17
BLW150	Albite	M13943 Amelia Courthouse, Virginia	Royal Ontario Museum	0.07
BLW178	Grey K-Feldspar	Britt, Ontario		0.12
BLW179	Pink K-Feldspar	Britt, Ontario		0.13
BLW188	Plagioclase	Loc HRW626, Britt, Ontario		5.70
BLW189	Plagioclase	Loc HRW626, Britt, Ontario		3.69
BLW219	Anorthite	Miakejima, Japan		1.03

*determined by X-ray-fluorescence analysis.

CHEMICAL SHIFT AND FELDSPAR STRUCTURES

The low-temperature plagioclase series

The ^{29}Si MAS nmr spectra (Fig. 1, Table 2) indicate at least three distinct structural types, corresponding to the albite structure, An_{0-10}, the *e*-plagioclase structure, An_{30-70}, and the anorthite structure, An_{90-100}. Across this series, low-field peaks between -82 and -90 ppm, corresponding to silicon atoms with higher *n* values in $^{29}Si(OAl)_n(OSi)_{4-n}$, increase in intensity.

Amelia albite gives three narrow, well-resolved ^{29}Si MAS nmr peaks, (Table 2; *cf.* Lippmaa *et al.* 1980), reflecting the high degree of Al–Si order in this structure.

Labradorite shows broad overlapping peaks, indicative of disorder, at -83, -88, -93, -99 and -105 ppm. Some spectra have an additional peak at -110 ppm, apparently due to $^{29}Si(OSi)_4$. The peaks that correspond to the chemical shifts in albite are assigned to silicon in sodic regions of the structure and those at -83 and -88 ppm to silicon in calcic zones.

The ^{29}Si MAS nmr spectrum of anorthite is resolved into three peaks (*cf.* Smith *et al.* 1983) narrower than those of labradorite and indicating less disorder. The peaks correspond to crystallographically distinct silicon sites surrounded by four AlO_4 tetrahedra.

Oligoclase gives a broadened albite-type ^{29}Si MAS nmr spectrum with an additional low-field peak at -86 ppm. This peak and the increased signal intensity of the peaks at -97 and -93 ppm are due to silicon in the calcic regions of the peristerite intergrowths (Smith 1974). Bytownite spectra seem to be a superposition of the labradorite and anorthite spectra, consistent with the presence of domains of each of these structures.

TABLE 2. DATA FOR SPECIMENS OF PLAGIOCLASE

Sample	% anorthite *	peak position (ppm)	nmr signal-to-noise ratio**
BLW150	0	-92.8, -97.1, -104.9	2.5
BLW036	9	-92.6, -96.8, -104.7	125
BLW128	13	-86.7, -92.6, -96.8, -100.2, -104.6	62.5
BLW080	57	-84.0, -88.8, -93.3, -99.0, -105.5, -111.1	50
BLW038	72	-83.6, -87.8, -93.3, -98.6, -105.6	100
BLW219	98	-82.7, -84.7, -89.3	125
BLW188	54	-90.6	5
BLW189	52	-90.6	5
BLW056	--	-95.5, -100.0	

* inferred by index of refraction
** 200 scans, 5 s relaxation delay between scans; 50 Hz line broadening

TABLE 3. DATA FOR SPECIMENS OF ALKALI FELDSPAR

Sample	peak position (ppm)	nmr signal-to-noise ratio*	modal composition
BLW004	-94.5, -96.8, -100.2	50	90% microcline 10% albite
BLW031	-92.4, -93.8, -96.8, -100.3, -104.1	12.5	60% microcline 30% quartz 10% albite
BLW123	-92.4, -94.5, -96.8, -100.3, -104.3	5	80% microcline 20% albite
BLW178	-93.2, -94.8, -97.2, -100.5, -104.4	50	99.5% microcline 0.5% opaques
BLW179	-93.2, -94.8, -97.2, -100.5, -104.4	50	99.5% microcline 0.5% hematite
BLW124	-94.6, -97.1, -100.2	12.5	87% microcline 10% albite 2% quartz 1% sericite
BLW083	-91.9, -96.3	25	70% orthoclase 20% albite 10% clays

* 200 scans; 5 s relaxation delay between scans; 50 Hz line broadening

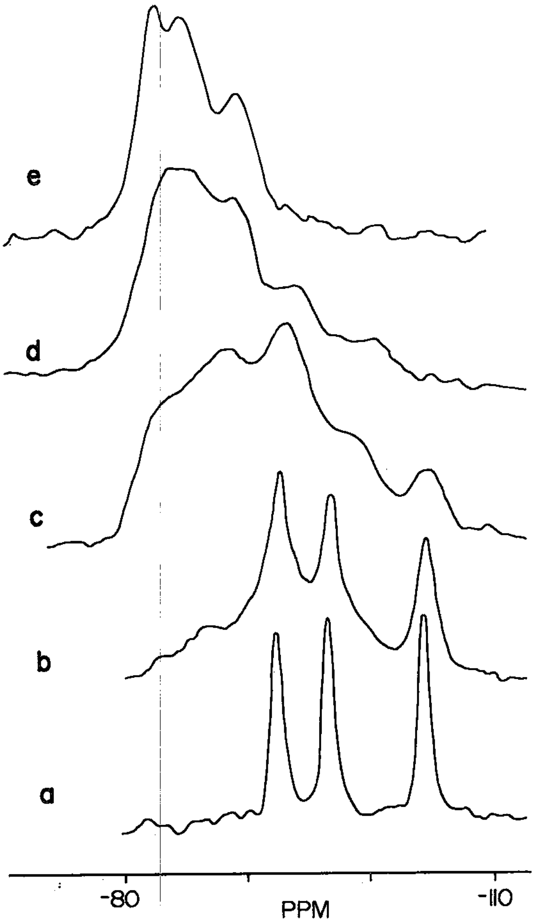

FIG. 1. ^{29}Si MAS nmr spectra of samples from the ordered plagioclase series: (a) An_0, Amelia albite (BLW150), (b) An_{13}, oligoclase (BLW128), (c) An_{57}, labradorite (BLW080), (d) An_{72}, bytownite (BLW038), (e) An_{98}, anorthite (BLW219).

The alkali feldspar series

The ^{29}Si MAS nmr spectra of albite and microcline each contain three peaks (Williams & Hartman 1983, Williams 1984, Smith *et al.* 1984). The perthite spectra have five peaks corresponding to a superposition of the albite and microcline spectra, with overlap of the central peak (Fig. 2, Table 3).

Low-temperature albite and microcline (both triclinic) have four T sites (Ribbe 1975). Most of the aluminum occupies the T_1O site in albite (Smith 1974) and in microcline (Ferguson 1980), leaving the T_1m, T_2O and T_2m sites for silicon. The low-field peaks at -92.5 ppm in albite and -95 ppm in microcline are allocated to the T_2m site, with two Si-O-Al linkages. The -96.8 ppm peak in albite and -97.0 ppm peak in microcline have been allocated by Smith *et al.* (1984) to the T_2O site and the -104.3 ppm peak in albite and the -100.4 ppm peak in microcline to the T_1m site on the basis of mean Si-O bond length, mean secant of Si-O-T angle and the total bond-strength of the oxygen atoms in the tetrahedra.

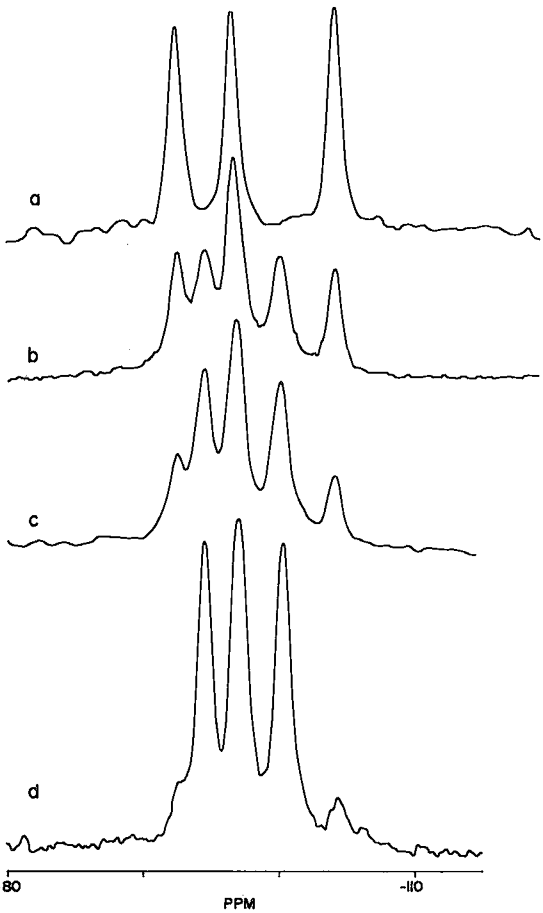

FIG. 2. ^{29}Si MAS nmr spectra of triclinic low-temperature alkali feldspars showing the resolution of both microcline peaks at -94.0, -97.0 and -100.4 ppm and albite peaks at -92.5, -96.8 and -104.6 ppm in perthite samples: (a) 100% albite (BLW150), (b) 30% albite, 70% microcline (BLW123), (c) 20% albite, 80% microcline (BLW124), (d) 10% albite, 90% microcline (BLW004).

High-temperature feldspars

Heating well-ordered microcline and plagioclase at 1100°C for up to 28 days causes progressive Al-Si disorder resulting in peak broadening (Fig. 3), such that the ^{29}Si MAS nmr spectra resemble those of natural high-temperature feldspars (Fig. 4). These results are consistent with those of Murdoch *et al.* (1983).

Natural specimens of orthoclase and disordered plagioclase give broad ^{29}Si MAS nmr signals (Fig. 4), with two maxima of equal intensity. In orthoclase these may be attributed to the two T sites, which are equally populated by silicon and aluminum (Smith 1974). The envelope of peaks, extending from -85 to -110 ppm, indicate a variety of environments for silicon with between zero and four Si-O-Al linkages,

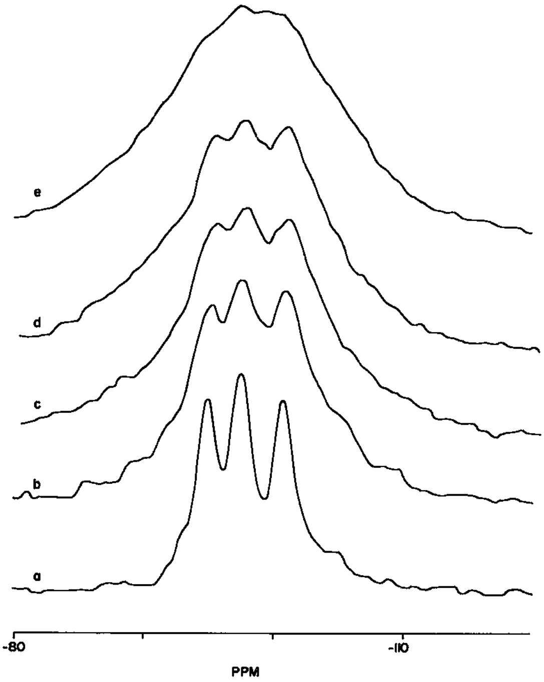

FIG. 3. ^{29}Si MAS nmr spectra of microcline heated at 1100°C: (a) initial spectrum, (b) after 8 days, (c) after 15 days, (d) after 20 days, (e) after 28 days.

and considerable Al–Si disorder throughout the structure.

THE EFFECT OF Fe^{2+} AND Fe^{3+} IMPURITIES

Peak widths and intensities can be greatly affected by the history of the sample. Most feldspars contain traces of iron, with Fe^{3+} substituting for Al^{3+} and Fe^{2+} substituting for Ca^{2+} (Smith 1974). Unaltered plagioclase and alkali feldspar with less than 0.1% total iron (determined by X-ray-fluorescence analysis) have a poor signal-to-noise ratio under standard conditions (200 scans; 5 s relaxation delay between scans). Much better spectra with especially sharp peaks are commonly obtained from such samples using much longer relaxation delays (*e.g.*, 300 s). Feldspars that have undergone slight alteration usually have 0.1 to 1.4% Fe, and give a good signal-to-noise ratio under our standard conditions. For example, oligoclase BLW036, with 0.16% Fe and approximately 1% sericite, gives well-resolved signals with the best signal-to-noise ratio (under standard conditions) of any feldspar studied by us. Feldspars with an iron content greater than 1.4% (*e.g.*, BLW188 and BLW189) give very poor spectral resolution, low signal-to-noise ratio and large spinning sidebands.

Because of the effectiveness of the large magnetic moment of the unpaired electron in inducing transitions among nuclear spin states, paramagnetic ions such as Fe^{3+} and Fe^{2+} can have pronounced effects on nmr spectra, notably in decreasing the ^{29}Si spin-lattice relaxation time, T_1 (Becker 1980, Barron *et al.* 1983, Watanabe *et al.* 1983). Long T_1 values are commonly a problem in solid-state nmr, as the nucleus being observed must relax between scans in order for repeated scanning of the spectrum to be effective (Wasylishen & Fyfe 1982). Thus the nature and amounts of paramagnetic species present can have a profound effect on nmr spectra. The above results confirm that the presence of some iron enhances feldspar ^{29}Si nmr spectra by relaxing the silicon atoms and allowing more rapid repetition of radiofrequency pulsing. However, too much iron causes peak broadening and loss of information, even though total intensity of the signal may continue to increase.

The effect of paramagnetic ions in broadening resonance peaks (Grimmer *et al.* 1983, Oldfield *et al.* 1983, Williams & Hartman 1983, Williams 1984) could obscure the broadening effect of next-nearest-neighbor *T*-site Al-Si disorder. To examine this possibility we carried out further studies of the effects of iron on peak width in microcline perthite and oligoclase samples. In such samples we find a pronounced dependence of peak width on relaxation delay between radiofrequency pulses (Table 4). Peak widths decrease as relaxation-delay increases. This is most readily explained if T_1 values are not uniform for a given silicon site throughout the structure. A short relaxation-delay favors observation of the signal from silicon atoms with short T_1 values. These T_1 values are presumably short owing to proximity to a paramagnetic centre, and the same proximity causes the peak broadening. We are apparently observing composite signals: the chemical shift stays the same but the peak width is related to distance from a paramagnetic centre.

TABLE 4. DEPENDENCE OF PEAK WIDTHS ON RELAXATION DELAY*

Relaxation delay (s)	Width at half height (Hz) of the peak at: -92.6 ppm	-96.8 ppm	-104.7 ppm
0.1	268	210	178
5.0	192	171	147
30.0	172	156	137
300.0	144	140	131

*oligoclase BLW036; 30° pulse; 50 Hz line broadening applied.

Spin diffusion, the predominant mode of spin-lattice relaxation in solids (Abragam 1961), is a process in which identical nuclei exchange spin states. It is highly efficient when the nuclei involved are close together but becomes much less efficient as the internuclear distance increases. It is apparently not efficient with dilute nuclei such as ^{29}Si (4.7% abundant); otherwise, all crystallographically equivalent silicon atoms would have the same T_1, and changes in peak width with relaxation delay would not occur. Recent work indicating that ^{13}C spin diffusion is inefficient in solids (Henrichs *et al.* 1984, Maiti & McGarvey 1984) is consistent with our interpretation.

Our results have important implications for ^{29}Si MAS nmr studies of minerals containing traces of

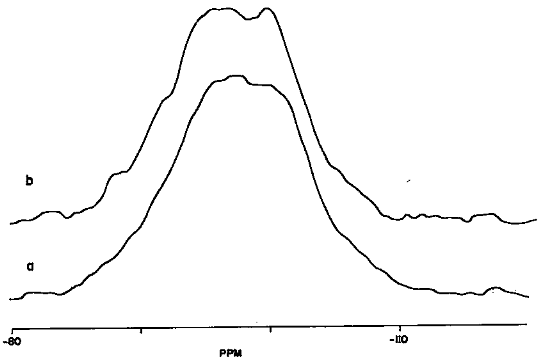

FIG. 4. ^{29}Si MAS nmr spectra of natural high-temperature feldspars: (a) labradorite from basalt from the Azores, (BLW056), (b) orthoclase from Nevada, (BLW083).

paramagnetic centres. The possibility exists that a spectrum may shed light only on silicon environments that have particularly short T_1 values, rather than being representative of the bulk sample. Indeed it may not be possible to specify a single T_1 value for such a sample, since a distribution of T_1 values could exist throughout the sample. Consistent with this, Higgins *et al.* (1984) found that their ^{29}Si relaxation data for zeolite ZSM-39 could not be fitted to a single value of T_1. Related problems of quantitative reliability in solid-state high-resolution nmr have been studied in detail for the case of ^{13}C cross-polarization MAS nmr of coals (Dudley & Fyfe 1982) and sludge (Pfeffer *et al.* 1984).

In liquids, ^{29}Si nmr suffers from the disadvantage of long spin-lattice relaxation times; these are generally reduced by the addition of small amounts of "relaxation reagents": paramagnetic substances such as tris(acetylacetonato)iron(III) (Harris *et al.* 1978). In solid aluminosilicates, trace paramagnetic impurities may normally act as a relaxation reagent and provide the principal mechanism of relaxation. Addition of Fe_2O_3 to samples of synthetic glasses in order to obtain spectra with a high signal-to-noise ratio (Fujio & Ogino 1984) is analogous to the use of a relaxation reagent in liquids, but with the major difference that in liquids all chemically equivalent silicon atoms are affected in the same way by paramagnetic ions, owing to rapid motion and time averaging. The situation is inherently more complex in solids. The use of very long relaxation delays, which would eliminate the ambiguity, is a very inefficient use of instrument time and is often not feasible.

The effect of inclusions and alteration

Inclusions of opaque minerals do not seem to affect significantly nmr resolution or signal strength; thus oligoclase BLW036 contains translucent plates of hematite and also black acicular opaque grains approximately 1 µm in length. The effect of the oxidation state of opaque phases was studied using samples from a single crystal of pegmatitic microcline approximately one metre in diameter. This sample is grey in the centre owing to the black needle-shaped inclusions (BLW178) and pink around the edge owing to the oxidation of the opaque needles to hematite (BLW179). There is no difference in signal strength or resolution between the ^{29}Si spectra of the two samples, suggesting that the signal comes from the bulk sample, remote from the inclusions.

Alteration of the feldspar or the presence of quartz or other inclusions does not have a measurable effect on the signal intensity, beyond that due to the decrease of the total feldspar content. Even where quartz is present as an appreciable fraction of the sample, its ^{29}Si nmr signal does not appear in our spectra, apparently owing to a very long spin-lattice relaxation time. This contrasts with the work of Smith & Blackwell (1983), who were able to obtain ^{29}Si MAS nmr spectra of SiO_2 polymorphs using a relaxation delay of only 10 s.

CONCLUSIONS

Although more work is required to define the quantitative reliability of the technique, ^{29}Si MAS nmr shows promise for the study of disorder and site occupancy in feldspars. The presence of a small amount of iron improves the efficiency of collection of feldspar ^{29}Si MAS nmr data, although care must be taken in the interpretation of such data.

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